928,276

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method of Producing an Iridised Pattern

We, CORNING GLASS WORKS, a Corporation organized under the laws of the State of New York, United States of America, of Corning, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the art of iridising and is concerned with the production of an iridised pattern on the surface of a refractory substrate. It is particularly concerned with an improved method for temporarily masking selected portions of the substrate surface to define a pattern of exposed surface for iridising.

In general, the well known art of iridising involves heating a glass or other refractory body to an elevated temperature, e.g. 500—700° C., and exposing a surface of the heated body to the vapours or atomised solution of a metal salt or other compound. Metal compounds suitable for iridising are those which hydrolyse and decompose, or otherwise undergo a chemical change, at the heated surface to form an adherent metal oxide film on the surface. A wide variety of metal compounds are described in the prior art as being suitable for this purpose including the chlorides, bromides, nitrates and acetates of such metals as tin, antimony, iron, bismuth, and zinc, and numerous metallo-organic compounds. Additional information as to suitable iridising materials and the manner in which they may be applied will be found in the patent literature such as Specification Nos. 340,371 and 639,561.

Iridised metal oxide films may be employed for either decorative or utilitarian purposes. Recently, a wide-spread interest has developed in the use of electroconductive metal oxide films of this type as resistance or heating elements on such articles as windshields, heating panels, warming trays and electrical resistors.

Frequently, it is desirable to pattern iridise, that is iridise only selected, localised areas of an article surface. Decorative patterns may be produced on a glass surface in this manner. Selective iridising has also been proposed as a means of producing conducting films or irregular shaped glass articles, such as a triangular or circular window, where it is desirable to obtain a uniform resistance across the iridised film, while employing terminal strips conforming to the edge or periphery of the article. A type of printed circuitry and numerous other electronic components may also be formed in this manner.

Iridised patterns may be produced by iridising an entire surface and then chemically removing the film in selected areas. It has also been proposed to mask temporarily, during application of the iridising material, those surface areas which are to remain uniridised. The latter is usually more convenient and desirable providing an effective masking material can be provided.

A suitable masking material should provide an effective barrier to the iridising material, should withstand the elevated temperatures employed in the iridising process, should not react with the glass or other surface which it masks, should be capable of easy application to the substrate surface and readily removable from that surface after iridising, should provide a sharply defined border for the exposed surface pattern, and should provide a continuous coating on the surface that is sufficiently adherent and cohesive to resist flaking, pinholing and mild abrasion.

Typical masking materials heretofore proposed include such ceramic materials as calcium salts, silica, and natural feldspars. Such materials are applied in paste form over the surface being masked and then dried. Surprisingly, these materials have not proved as

[*Price* 4*s.* 6*d.*]

satisfactory as might be expected. In particular, it has been found difficult to avoid pinholes, cracks, flaking, porosity and other sources of coating discontinuities which render the coating ineffective as an iridising mask. On the other hand, even a slight amount of flux impurity, such as alkali, may produce a surface reaction or fusion at iridising temperatures that seriously interferes with subsequent removal of the coating. Also it is not always possible to obtain as sharply defined a pattern as is desired. Ordinarily masking tape materials, of course, are generally incapable of withstanding the elevated temperatures involved. It is the purpose of this invention to provide an improved method for producing iridised patterns on a refractory substrate. A further purpose is to provide an improved masking material and method of masking portions of a surface in the production of iridised patterns.

The invention provides a method for producing an iridised pattern on a refractory substrate surface which comprises applying a metal masking coating in the form of a liquid suspension of metal particles which outlines a pattern of exposed substrate surface corresponding to the desired iridised pattern, substantially volatilising the liquid vehicle, thereafter forming an iridised film over the exposed surface and subsequently removing the metal coating.

The particular metal employed must be physically and chemically stable at the temperatures employed for iridising and must also be substantially inert with respect to the substrate material. Within these general limits any metal or alloy may be employed, the noble metals and ferrous type metals being particularly suitable. It has been found that silver provides a particularly effective mask and is readily available in a convenient form for application.

For masking purposes the metal is subdivided into either powder or flake form and suspended in a vehicle to provide a mixture of paint-like consistency. Commercial silver paint suspensions are well adapted to this purpose, and example of such paint material being sold by the Hanovia Chemical and Manufacturing Co. under the Registered Trade Mark "Hanovia 220U" Where a commercial preparation is not available, the subdivided metal may be suspended in a suitable organic vehicle such as a fatty oil, turpentine, an alcohol or mixtures of such known organic vehicles to provide a suspension of suitable consistency. It will be understood that the particular proportions of metal and vehicle selected will depend upon the particular vehicle employed and the manner of applying the suspension on the surface. Ordinarily the vehicle will either volatilise during drying or decompose on heating of the substrates preparatory to the iridising operation.

A metal suspension may be applied to the substrate surface in any of the well known coating procedures. For example, it may be sprayed on the surface utilising a suitably configured stencil. A particularly effective procedure is to apply the suspension through a silk screen in accordance with conventional decorating practice. This provides a sharply defined pattern of any pre-determined configuration on the surface of the article.

It has been found that a coating of metal masking material may provide an effective barrier to iridising materials even through underfired and hence relatively soft and porous. This is especially desirable since it avoids a separate firing step and also facilitates subsequent removal. It has further been found that penetration of metal chloride iridising solutions does not occur even in the presence of minor discontinuities such as small pinholes or hair lines in the metal film. While the exact explanation of this desirable situation is not known, it appears that a chemical complexing action may occur to render the metal film self-healing.

In practising the invention, an article to be pattern iridised is initially metallised, as described above, on those predetermined surface areas that are to remain clear and uniridised in the finished product. The metal coating provides a mask which outlines exposed portions of the substrate surface that are to be iridised. The article is then heated to a suitable iridising temperature, e.g. 600° C. While only the exposed surface need be treated with an iridising solution, it is ordinarily more convenient to apply the iridising material over the entire article surface including both exposed and masked portions. This is particularly true where the material is being sprayed or fumed on to the article. Customarily metal chloride salts are employed either in vapour or solution form for iridising purposes, although, as indicated earlier, a wide variety of inorganic and organic metal compounds are known to be suitable for iridising purposes. In producing electroconductive films, it is generally preferred to employ a tin chloride for iridising and to mix with the tin chloride a minor proportion of antimony chloride to modify the resistivity as described in Specification No. 639,561. In any event the selected iridising material is applied to the heated article surface and undergoes a chemical change whereby a corresponding metal oxide film is formed on the surface. The article, having an adherent, iridised, metal oxide film formed on its exposed surface is then cooled and the metal masking coating removed to produce an iridised pattern surrounded by exposed or clear substrate surface. Either an acid or mild caustic solution may be employed for removing the metal. Generally speaking, it is desirable to employ a material which is chemically inert with respect to the iridised film thus

permitting immersion of the article. It has been found that an ammonium bifluoride solution is particularly effective in removing masking metals and that a silver masking coating may be readily washed off with such solution while the iridised film is unaffected.

The resulting article, bearing an iridised pattern on its surface, may then be further processed if necessary. For example, in producing resistance or circuit elements, conducting terminals or bus bars may be applied along the edge or periphery portions of the iridised film.

WHAT WE CLAIM IS:—

1. A method for producing an iridised pattern on a refractory substrate surface which comprises applying to pre-determined portions of such surface a metal masking coating in the form of a liquid suspension of metal particles which outlines a pattern of exposed substrate surface corresponding to the desired iridised pattern, substantially volatilising the liquid vehicle, thereafter forming an iridised film over the exposed surface and removing the metal coating.

2. A method as claimed in Claim 1 wherein the metal masking material consists of silver.

3. A method as claimed in Claim 1 or 2 wherein the metal masking material is removed by washing with a solution of ammonium bifluoride.

4. Refractory substrates having an iridised pattern on the surface thereof when produced by the method claimed in any one of the preceding claims.

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